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SHORT COMMUNICATIONS

Unusual Intramolecular Assistance in the Functionalization of the Side-Chain Double Bond of 5-Allyl-2,3,5-trichloro-4,4-dimethoxy-2-cyclopentenone in the Reaction with Iodine

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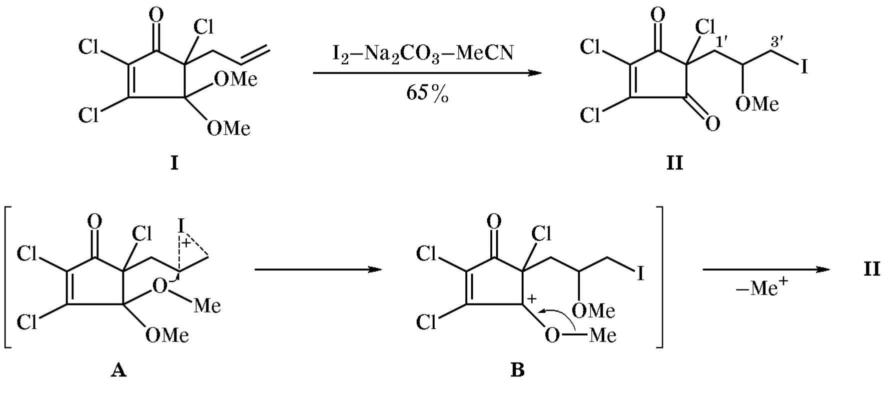
By reaction of trichlorocyclopentenone **I** [1] with 2.5 equiv of I_2 in acetonitrile containing Na_2CO_3 we obtained iodomethoxy derivative **II** in 65% yield (Scheme 1). The reaction result can be regarded as an unusual example of intramolecular migration of one methoxy group in ketone **I** to the terminal double bond with simultaneous addition of iodine atom and deprotection of the acetal moiety.

The ^{13}C NMR spectrum of cyclopentenedione **II** contains different signals from the carbonyl carbon atoms (δ_C 184.74 and 186.33 ppm) and carbon atoms at the double bond (δ_C 147.34 and 150.51 ppm) with approximately equal intensities. The other carbon atoms of **II** each give a strong single signal. The observed diastereotopicity of the prochiral cyclic fragment of **II** is likely to originate from steric interactions which restrict rotation about the $C^{1'}-C^{2'}$ bond. A plausible mechanism of the above transformation includes intramolecular elimination of the methoxy group in intermediate **A** with subsequent loss of methyl cation from intermediate **B** (Scheme 1).

2,3,5-Trichloro-2-(3-iodo-2-methoxypropyl)-2-cyclopentene-1,3-dione (II). To a solution of 150 mg (0.525 mmol) of compound **I** in 4 ml of CH_3CN we added 560 mg (5.25 mmol) of Na_2CO_3 and 670 mg (2.62 mmol) of I_2. The mixture was stirred for 1 h in the dark, 5 ml of diethyl ether was added, and the mixture was treated with a 10% solution of $Na_2S_2O_3$. The organic layer was separated, washed with a saturated solution of NaCl, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by column chromatograpy on silica gel to isolate 120 mg (65%) of product **II**. mp 97.5–99°C, R_f 0.64 (hexane–ethyl acetate, 5 : 1). IR spectrum, ν, cm^{-1}: 840, 1610, 1740, 1770. ^1H NMR spectrum, δ, ppm: 2.61 d.d (1H, 1′-H, J = 14.00, 4.3 Hz), 2.69 d.d (1H, 1′-H, J = 14.00, 9.9 Hz), 3.00 d.d.d.d (1H, 2′-H, J = 4.2, 4.3, 9.9, 5.6 Hz), 3.48 d.d (1H, 3′-H,

Scheme 1.



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J = 11.0, 4.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 6.85 (CH_2I), 42.07 (CH_2), 55.50 (OCH_3), 61.03 (C^2), 74.46 (CHO), 147.34 and 150.51 (C^4, C^5), 184.74 and 186.33 (C^1, C^3). Mass spectrum (electron impact), m/z (I_{rel}, %): 396 (54) $[M]^+$, 361 (75) $[M-Cl]^+$, 325 (63) $[M-Cl-HCl]^+$, 269 (83) $[M-I]^+$, 233 (27) $[M-Cl-I]^+$, 219 (100) $[M-Cl-CH_2I]^+$, 141 (25) $[CH_2I]^+$, 128 (21) $[HI]^+$ 127 (29) $[I]^+$, 87 (88) $[ClC\equiv CC=O]^+$. Found, %: C 27.40; H 2.14; Cl 26.20; I 30.92. $C_9H_8Cl_3IO_3$. Calculated, %: C 27.20; H 2.03; Cl 26.76; I 31.93.

The IR spectrum was measured on a UR-20 spectrophotometer (film). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 MHz for ^{1}H and 75.47 MHz for ^{13}C; acetone-d_6 was used as solvent, and TMS, as internal reference. TLC was performed on Silufol plates. The mass spectrum (70 eV) was obtained on an MKh-1320 instrument; ion source temperature 60–90°C, direct sample admission; the spectrum was reduced to monoisotope form with respect to ^{35}Cl, ^{12}C, and ^{16}O.

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